HIGH-STRENGTH, HEAT-RESISTANT ALLOY FOR EXHAUST VALVES WITH IMPROVED OVERAGING-RESISTANCE

BACKGROUND OF THE INVENTION

Field in the Industry

The present invention concerns a high-strength, heat-resistant alloy for exhaust valves with improved overaging-resistance. The alloy is also suitable for a material of meshes used in exhaust gas treatment catalyst, and therefore, the phrase "for exhaust valves" should be interpreted not as limiting but an example of use.

Prior Art

Before, as a material for exhaust valves of engines SUH35 steel has been used. Recent strict regulation on exhaust gas, however, increased load on the valves and sometimes JIS SUH35 is considered to be dissatisfactory due to the relatively low strength thereof. Thus, there has arisen demand for valve materials having higher strength, and to meet the demand, Ni-based alloys such as JIS NCF751 came to be chosen. Because the Ni-based alloys are expensive, they are used only for high performance engines. In order to make the price of valve materials lower

research and development have been made on various alloys with decreased Ni-content.

The assignees have been developing valve materials solely or jointly for many years and disclosed various kinds of alloys and technologies for heat-treating them. The following reviews a brief history of our development.

Japanese Patent Disclosure (hereinafter referred to as "JPD") Sho.56-20148 discloses an alloy for exhaust valves which consists of C: 0.01-0.20%, Si: up to 2.0%, Ni: 25-50%, Cr: 13-23%, Ti: 1.5-3.5%, Al: 0.1-1.5% and the balance of Fe. In this alloy good high-temperature strength and corrosion resistance are ensured by solution treatment and aging treatment to precipitate γ'-phase, $Ni_3(Al, Ti)$, in austenitic matrix. Though the claimed ranges of Ti- and Al-contents are broad, the ratios of Ti/Al in the working examples were so high as 2.8-7.8, which made the γ'-phase unstable and precipitation of η-phase was observed.

This problem was solved by JPD Sho.58-34129, which disclosed the process of treatment of the alloy having the above-defined composition, which comprises pre-heat treatment at 700-975°C, hot working at a temperature of 975°C or lower, and solution- and aging-treatment at a temperature of 975°C or lower, to give better high-temperature property, particularly, tensile strength, and fatigue strength.

JPD Sho.60-13020 also disclosed a process for heat treating a valve alloy. The process is characterized by homogenizing an Fe-Ni-based alloy in which γ′-phase may precipitate at a temperature higher than the recrystalisation temperature, giving distortion by processing at a temperature lower than the recrystalisation temperature, and subjecting the processed material to aging treatment to accelerate intragranular precipitation of the γ′-phase and to suppress precipitation of the η–phase, Ni_3Ti, at grain boundaries. Thereafter, JPD Sho.60-13050 disclosed an invention which, in the above-described Ni-Fe-based alloy, prevents deposition of η–phase, which is harmful to the strength and notch-sensitivity, by addition of suitable amounts of B (0.001-0.05%) and Al (0.1-0.7%).

JPD Sho.60-46343 disclosed an alloy for valve material which, using the basic alloy components of C: 0.01-0.15%, Si: up to 2.0%, Mn: up to 2.5%, Ni: 35-65%, Cr: 15-25%, Mo: 0.5-3.0%, Nb; 0.3-3.0%, Ti: 2.0-3.5%, Al: 0.2-1.5% and B: 0.001-0.020%, contains a suitable amount or amounts of one or more of Mg, Ca and REM with the balance of Fe. The material, which is relatively high-alloyed, has the resulting merits of improved high-temperature strength and corrosion resistance, and further, good hot workability.

JPD Sho.60-162760 concerns a technology in the genealogy of the above-described JPD Sho.60-13020

which is characterized in that an Ni-based alloy comprising the basic alloy components of C: 0.01-0.20%, Cr: 13-23%, Ti: 1.5-3.5% and Al: 0.1-4.5%, provided that (Ti+Al): 2.0% or more, is treated at a high temperature above the γ'-solvus temperature, work-hardened by reduction of 20% or more at a temperature below the recrystalization temperature, and age-hardened at 600-850°C. The product produced by this process has high strength and high toughness.

On the other hand, JPD Sho.60-211028 proposed an alloy composition for exhaust valves with good high temperature corrosion resistance, particularly, resistance to $PbO+PbSO_4$-corrosion, which comprises C: 0.01-0.15%, Si: up to 2.0%, Mn: up to 2.5%, Ni: 53-65%, Cr: 15-25%, Nb: 0.3-3.0%, Ti: 2.0-3.5%, Al: 0.1-1.5%, B: 0.001-0.020% and the balance of Fe.

JPD Sho.61-119640 disclosed an Ni-based heat resistant alloy with enhanced high temperature strength and good hot workability, which comprises C: 0.01-0.15%, Si: up to 2.0%, Mn: up to 2.5%, Cr: 15-25%, Mo+1/2W: 0.5-5.0%, Ti: 1.5-3.5%, Al: 0.5-2.5%, B: 0.001-0.020%, Fe: up to 5% and the balance of Ni.

Further known technologies are disclosed in JPD Sho.58-34129, JPD Hei.7-109539, JPD Hei.7-216482, JPD Hei.9-279309 and JPD Hei.11-229059. Of the alloys disclosed in these JPD's, those in JPD Sho.58-34129 and JPD Hei.7-216482 contain high amounts of Ni and are still expensive, in other words, cost reduction is

not sufficient. Though JPD Hei.7-109539, in which Ni-content is so decreased to be at highest 49%, realized low cost, the alloy is not fully satisfactory because of its low hot workability. The reason for the low hot workability seems to be due to high Al-content. The alloy disclosed in JPD Hei.9-279309 exhibits high strength. However, the high strength can be maintained only for a short period that it decreases significantly when used for a long period at a high temperature, and thus, the overaging-resistance of the alloy is inferior. Also, the alloy of JPD Hei.11-229059 has a weak point of low hot workability, which seems to be caused by high Al-content.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a novel heat resistant alloy for exhaust valves wherein the Ni-content is limited to maximum 62%, wherein the strength is equal to or even higher than that of the conventional Ni-based alloys for exhaust valves and wherein the strength is maintained even after use for a long period at a high temperature.

The high strength, heat resistant alloy for exhaust valves according to the present invention achieving the above-mentioned object consists essentially of, by weight %, C: 0.01-0.2%, Si: up to 1%, Mn: up to 1%, P: up to 0.02%, S: up to 0.01%, Ni:

30-62%, Cr: 13-20%, W: 0.01-3.0%, Mo: up to 2.0%, provided that Mo+0.5W: 1.0-2.5%, Al: 0.7% or higher and less than 1.6%, Ti: 1.5-3.0%, Nb: 0.5-1.5%, B: 0.001-0.01%, provided that [%Ti]/[%Al]: 1.6 or more and less than 2.0, and the balance of Fe and inevitable impurities.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The heat resistant alloy for exhaust valves according to the present invention may contain, in addition to the above mentioned basic alloy components, one or more of the components of the following three groups:

I) one or more of Mg: 0.001-0.03%, Ca: 0.001-0.03% and Zr: 0.001-0.1%,

II) Cu: up to 2.0%,

III) V: 0.05-1.0%.

The effects of the alloy components and the reasons for limiting the alloy compositions as defined above will be explained below in regard to both the essential components and the optional components.

C: 0.01-0.2%

Carbon enhances the high temperature strength of the matrix by forming carbides with Cr, Ti, Nb and Ta. To obtain this effect carbon of 0.01% or more is essential. Too much carbon causes formation of too much carbides, which affect hot- and cold-workability

as well as ductility and toughness of the alloy. Thus, 0.2% is set to be the upper limit.

Si: up to 1.0%

Silicon is added as a deoxidizing agent at the time of melting and refining the alloy. Addition of a small amount of Si effective as the deoxidizing agent may cause no problem. Because addition of much amount of Si decrease the toughness and workability of the alloy, the amount of Si should be up to 1.0%.

Mn: up to 1.0%

Manganese, which also effects as a deoxidizing agent like silicon, may be added upon necessity. Addition in much amount will damage the workability and high temperature oxidation resistance, and the amount of Mn to be added is chosen in the range up to 1.0%.

P: up to 0.02%

S: up to 0.01%

Because the Ni-amount is limited in this alloy, ranges of workable conditions in hot working are narrow. Therefore, the alloy designing should be so carried out that the hot workability becomes high. It is preferable that the contents of P and S, which are inevitable impurities damaging the hot workability, are as low as possible. Both the above values are the allowable limits.

Ni: 30-62%

Nickel is an element to form austenite. It is

an essential component for ensuring the heat resistance and corrosion resistance, and further, for forming γ'-phase, which is a precipitation strengthening phase. Unless the Ni-content is 30% or higher the strength and the phase stability are insufficient and the hot-workability is low. Because too much addition results in increase of manufacturing cost, the upper limit is, as explained above, set to be 62%. Preferable range based on the balance of the performance and the cost of the alloy is 30-54%, more preferably, 35-54%.

A part of Ni, up to 5% of the alloy, can be replaced with Co. Replace of Ni with Co gives a merit of enhanced creep strength. However, it is not advisable to add much Co, not only because Co is more expensive than Ni and addition of a large amount causes increase in the cost, which is against the aim of the invention, but because a large amount of Co lowers the stability of γ'-phase.

Cr: 13-20%

Chromium is an element essential for ensuring heat resistance of the alloy, and Cr of at least 13% is necessarily added. If, however, Cr is added in an amount exceeding 20%, σ-phase will precipitate to lower the toughness and high temperature strength. Preferable amount of Cr-addition is up to 18%.

W: 0.01-3.0%

Tungsten has the effect of improving the high

temperature strength of the alloy by solution strengthening. To obtain this merit it is recommended to add a suitable amount of 0.01% or higher. Excess addition results in increase of the cost and decrease of the workability, and therefore, the addition amount should be chosen in the range up to 3.0%.

Mo: up to 2.0%

Molybdenum also improves, likewise W, the high temperature strength of the alloy by solution strengthening, and it is recommended to add a suitable amount of Mo. Because Mo is also so expensive that addition of a large amount causes increased cost, and because it decreases workability, the amount of Mo-addition is chosen in the range up to 2.0%.

Mo+0.5W: 1.0-2.5%

As is well known, in case of mixed use of Mo and W the value of Mo+0.5W, Mo-equivalent (hereinafter abbreviated as "Mo-eq."), is discussed. In order to obtain this merit certainly, addition of Mo in the amount corresponding to Mo-equivalent of 1.0% or more is recommended. The upper limit of the Mo-eq. is set to 2.5%.

Al: 0.7% or more and less than 1.6%

Aluminum is an important element which couples with Ni to form γ'-phase. If the amount of Al is less than 0.7%, precipitation of γ'-phase will be insufficient and the high temperature strength may not be obtained. On the other hand, addition of 1.6% or

higher will lower the hot workability.

Ti: 1.5-3.0%

Titanium, like Al, Nb and Ta, reacts Ni to form the γ′-phase which is effective in enhancing the high temperature strength of the alloy. In case of Ti-amount of less than 1.5%, solution temperature of γ′-phase becomes low, and therefore, sufficient high temperature strength will not be obtained. On the other hand, in case of excess addition of Ti over 3.0% causes decreased workability and tendency of deposition of η-phase (Ni_3Ti), which decreases the high temperature strength and the toughness.

%Ti/%Al: 1.6 or more and less than 2.0

Strength of this kind of alloy is given by age-hardening caused by uniform and fine precipitation and distribution of γ′-phase. It has been discovered that the precipitation amount and the phase stability of the γ′-phase depend on the Ti/Al ratio in the alloy. If %Ti/%Al is so high as 2.0 or more, γ′-phase becomes unstable and η-phase may precipitate to lower the strength. This is the phenomenon of "overaging". In order to avoid precipitation of the η-phase and to obtain overaging-resistance, it is necessary to keep this ration less than 2.0. On the other hand, it is not desirable that the ratio becomes such a low level as less than 1.6, because the initial strength of the alloy will be low.

Nb: 0.5-1.5%, preferably, 0.6-1.5%

Niobium is a γ'-phase forming element, and formation of γ'-phase enhances the strength of the alloy. To achieve this effect, 0.5% or more, preferably, 0.6% or more of Nb must be added. However, too much addition must be avoided due to decrease of the toughness, and 1.5% is the upper limit from this reason. A part of Nb may be replaced with Ta which has the same behavior as Nb. Therefore, the above-mentioned range of Nb-content should be understood as that of Nb+Ta.

B: 0.001-0.010%

Effects of adding B are contribution to improvement in the hot workability, suppression of formation of η-phase which prevents decrease of high temperature strength and the toughness, and enhancement of high temperature creep strength. These effects can be obtained at such a low content as 0.001%, while addition of B exceeding 0.01% is too much and lowers the melting point of the alloy resulting in damaging the hot workability of the alloy.

One or more of Mg: 0.001-0.03%, Ca: 0.001-0.03% and Zr: 0.001-0.100%

Both Magnesium and Calcium are the elements having deoxidizing and desulfurizing effects, and heighten the cleanness of the steel and segregate at the grain boundaries to strengthen the boundaries. These effects can be obtained at such a low addition amount each as 0.001%. On the other hand, addition in

a large amount or amounts will lower the hot workability, and thus, each 0.03% is the upper limit for both the elements.

Zirconium has, like B, the effect of increasing the creep strength of the alloy. Addition of 0.001% or more is effective, and addition exceeding 0.1% causes decrease of the toughness.

Cu: up to 2.0%

In diesel engines sulfate corrosion caused by sulfur contained in fuels may be a problem. Existence of Cu in the alloy is useful for giving resistance to the sulfate corrosion to the alloy, and is meaningful depending on the kinds of use of the valve alloy. Cu further contributes to oxidation resistance. Too much addition decreases the hot workability, and an addition amount up to 2.0% is chosen.

V: 0.05-1.00%

Vanadium is, like Mo and W, effective as solution strengthening element. It also has the effect of stabilizing MC-type carbides. Therefore, addition of V of 0.05% or more is recommended. Too much addition exceeding 1.0% will lower the toughness of the alloy.

The heat resistant alloy for exhaust valves according to the present invention can be produced at a lower cost due to the Ni-amount limited to maximum 62%. Nevertheless, as seen from the data of the Examples described below, the alloy exhibits the

strength higher than those of the conventional alloys containing equal or even much more amount of Ni. The problem of tendency of overaging in the prior technologies was dissolved by the invention which chose the Ti/Al ratio in a lower range. Excellent hot workability is also a characteristic feature of the alloy of the invention. This was enabled by the alloy composition in which Mo-eq. or the value of Mo+0.5W is suppressed to relatively low, and in turn, the content of Fe, which is favorable to the workability, is kept high.

As noted before, though the present alloy is suitable as a material for exhaust valves of gasoline engines and diesel engines, it is also useful for other various uses in which the properties similar to those required for the valves, namely, hot workability, overaging-resistance and high strength, are required.

EXAMPLES

Heat resistant alloys for exhaust valves having the alloy compositions shown in Table 1 (Working Examples) and Table 2 (Control Examples) were produced in a high frequency induction furnace, and cast into ingots. Of the Control Alloys, the alloys of No.1, No. 2, No.3 and No.4 are the alloys of the above-mentioned JPD Sho.60-46343, JPD Sho.60-211028, JPD Sho.58-34129 and JPD Hei.9-279309, respectively. The ingots of the

alloys were forged and rolled to round rods of diameter 16mm. The rods were subjected to solution treatment of heating at 1050°C for 1 hour followed by water cooling, and aging treatment of heating at 750°C for 4 hours followed by air cooling.

The samples thus prepared were then tested by room temperature tensile tests, high temperature high speed tensile tests and high temperature tensile tests. Also, the samples were subjected to measurement of Rockwell hardness and rotation bending fatigue strength. The results are shown in Table 3 (Working Examples) and Table 4 (Control Examples).

The testing methods are as follows:

[Room Temperature Tensile Tests]

This was done in accordance with the method defined in JIS Z 2241.

[High temperature High Speed Tensile Tests]

The tests were carried out at different temperatures in the range of 800-1250°C with intervals of 50°C, at tension rate of 50 mm/sec. As the measure of the hot workability, the temperature ranges in which reduction of 60% or higher was obtained were determined.

[Rotation Bending Fatigue Tests]

Using the samples, which were separately subjected to aging treatment of heating at 800 °C for 400 hours followed by air cooling, measurement of Rockwell hardness and rotation bending fatigue tests

were carried out. The results are shown in Table 5 (Working Examples) and Table 6 (Control Examples).

From the data in Tables 3-6 it is understood that the samples of Working Examples A-H according to the present invention showed good results in all the properties tested with desirable balance, while the Control Examples, which are out of the scope of the invention, contain some problems. Control No.1 has no good workability at high temperature. Control No.2 showed, notwithstanding the low %Ti/%Al ratio, high initial strength (room temperature strength), owing to the fact that Mo-eq. is high. Instead, it has too high hardness and low hot workability. Control No.3 has low hot workability. Control No.4 is dissatisfactory because of insufficient fatigue strength. Control No.5 is short of hardness.

As one of the practical properties required for the exhaust valve material, forgeability is important. More specifically, broad temperature range in which forging can be done is desired. It is requested that the temperature range in which reduction of 60% or more is achieved in high speed, high temperature tensile tests is 250°C or broader. The temperature ranges obtained in the Working Examples according to the invention are 250-300°C, while the ranges obtained in the Control Examples are narrower. The reason why the temperature range is particularly narrow in Control No.2 (175°C) is attributed to the high Mo-eq.,

3.5%. In Control No.4, which satisfies the condition of the temperature range 250°C or broader is, as pointed out above, short of the strength.

TABLE 1 Alloy Compositions (Working Examples)

No.	C	Si	Mn	P	S	Ni	Cr	Mo	W	Al	Ti	Nb+Ta	B	Mg,Ca,Zr	Cu	V	Fe	Ti/Al
A	0.05	0.12	0.11	0.002	0.001	50.2	16.2	1.2	0.5	1.42	2.62	1.25	0.003	-	-	-	26.3	1.85
B	0.03	0.21	0.15	0.001	0.001	60.4	15.0	1.6	1.1	1.37	2.38	1.48	0.002	-	-	-	16.3	1.74
C	0.06	0.46	0.29	0.001	0.002	39.3	17.8	1.6	1.6	0.92	1.81	1.49	0.005	Zr 0.04	-	-	34.0	1.97
D	0.04	0.10	0.09	0.002	0.001	53.7	17.4	0.5	1.8	1.39	2.70	0.83	0.003	Zr 0.05	0.83	-	20.6	1.94
E	0.05	0.13	0.16	0.001	0.001	47.5	15.9	0.9	0.9	1.47	2.45	1.30	0.004	Mg 0.002	-	-	29.2	1.67
F	0.03	0.19	0.23	0.002	0.001	45.0	14.3	0.4	2.4	1.28	2.54	1.17	0.002	Mg 0.002 Ca 0.001 Zr 0.03	0.26	-	32.2	1.98
G	0.05	0.11	0.18	0.001	0.001	32.6	14.8	0.5	1.2	1.35	2.61	1.38	0.006	Mg 0.002 Ca 0.001	-	-	45.2	1.93
H	0.04	0.20	0.19	0.001	0.001	51.1	15.5	0.6	1.5	1.41	2.47	1.42	0.003	-	-	0.6	25.0	1.75

TABLE 2 Alloy Compositions (Control Examples)

No.	C	Si	Mn	P	S	Ni	Cr	Mo	W	Al	Ti	Nb+Ta	B	Mg,Ca,Zr	Cu	V	Fe	Ti/Al
1	0.03	0.20	0.19	0.001	0.001	65.0	17.8	1.5	1.0	1.41	2.58	1.21	0.004	Mg 0.002	-	-	9.1	1.83
2	0.04	0.10	0.08	0.001	0.001	59.8	15.0	1.7	3.6	1.68	2.52	1.60	0.003	-	-	-	13.9	1.50
3	0.06	0.16	0.51	0.001	0.001	40.6	17.8	2.1	0.1	0.75	2.38	1.07	0.003	-	-	-	34.6	3.17
4	0.03	0.21	0.19	0.001	0.001	32.2	15.8	-	-	1.16	2.67	0.84	0.003	Mg 0.002	-	-	46.9	2.30
5	0.05	0.15	0.17	0.001	0.001	52.5	16.9	1.2	0.4	1.79	2.42	0.55	0.005	-	-	-	23.9	1.35

TABLE 3 Results 1 (Working Examples)

No.	Room Temp. Tensile Strength (MPa)	Temperature Range * (℃)	Rockwell Hardness (HRC)	Tensile Strength at 800 ℃ (MPa)	10^7 Rotating Bending Fatigue Strength (MPa)
A	1283	275	37.8	681	322
B	1295	300	36.5	716	341
C	1237	275	32.3	492	283
D	1279	275	36.2	690	330
E	1256	275	35.9	669	308
F	1250	275	35.7	634	299
G	1271	250	36.0	643	302
H	1284	275	37.4	695	337

* The temperature ranges were determined by the high temperature, high speed tensile tests at reduction of 60% or more.

TABLE 4 Results 1 (Control Examples)

No.	Room Temp. Tensile Strength (MPa)	Temperature Range * (℃)	Rockwell Hardness (HRC)	Tensile Strength at 800 ℃ (MPa)	10^7 Rotating Bending Fatigue Strength (MPa)
1	1292	225	38.0	726	358
2	1321	175	41.1	778	375
3	1240	200	32.9	425	214
4	1218	250	32.2	425	236
5	1193	275	31.9	537	302

* The temperature ranges were determined by the high temperature, high speed tensile tests at reduction of 60% or more.

TABLE 5 Results 2 (Working Examples)

No.	Rockwell Hardness (HRC)	10^7 Rotating Bending Fatigue Strength (MPa)
A	34.5	306
B	33.1	321
C	31.6	250
D	33.2	313
E	32.8	298
F	32.8	288
G	32.0	262
H	34.3	313

TABLE 6 Results 2 (Control Examples)

No.	Rockwell Hardness (HRC)	10^7 Rotating Bending Fatigue Strength (MPa)
1	35.1	334
2	37.4	340
3	28.6	186
4	31.8	242
5	31.9	265